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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for the Preparation of Trioxane

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Abstract of the disclosure:

Process for the preparation of trioxane

Trioxane can be obtained with a minimum energy requirement if acetal polymers are broken down in the presence of water and an acid catalyst. The process represents a contribution to waste disposal and environmental protection.

Description

Process for the preparation of trioxane

5 The invention relates to a process for the preparation of trioxane from homo- and/or copolymers of formaldehyde in the presence of acid catalysts.

10 The preparation of trioxane from aqueous formaldehyde solutions is described in various instances in the literature (cf. Walker, Formaldehyde, Reinhold Publ. New York, 3rd edition, 1964, pages 198-199).

15 Trioxane (TOX) is formed from aqueous formaldehyde at relatively high temperatures in the presence of acid catalysts and is removed from the reaction mixture by distillation. The synthesis vapor is usually worked up in a rectifying column mounted on the reactor (US Patent 2,304,080). The trioxane-rich phase is subjected to extraction and/or another separation process. To achieve high space-time yields, the reaction is carried out in a forced circulation evaporator (Canadian Patent 20 1,125,774). The copolymers obtained by trioxane copolymerization are of a high quality and belong to the field of industrial plastics.

25 Industrial plastics are processed by extrusion or injection molding, product waste being formed, which must be disposed of. Sprues and burrs are produced during processing by injection molding. Extruded goods are mostly machined, up to 50% of the material not infrequently being obtained as waste. Materials which do not always conform to type are also sometimes formed 30 during the production process and must be disposed of. Incineration and landfill have to date been available as methods of disposal. A recycling process is therefore to be preferred.

- A process for generating gaseous formaldehyde from polyoxymethylene, such as paraformaldehyde, is known (US-A 3,883,309). In this process, a dispersion of polymeric formaldehyde is decomposed thermally at 100 - 300°C to give formaldehyde, and this is separated off in gaseous form. This process is extremely complicated and requires considerable technical effort to prevent blockages due to paraformaldehyde. If copolymers are used, contamination of the formaldehyde by comonomers cannot be excluded.
- 10 The object of the present invention was to find a process which, inter alia, enables polyacetal to be recycled without displaying the difficulties mentioned, producing a material which can be used again directly for copolymerization.
- 15 This has been achieved by a process for the continuous preparation of trioxane from formaldehyde, in which an acetal polymer is broken down in the presence of water and an acid catalyst and the formaldehyde formed is converted into trioxane in the same process step.
- 20 High trioxane concentrations in the synthesis vapor which correspond to those of the maximum equilibrium which can be achieved using formaldehyde solutions are obtained by the process according to the invention.
- 25 The preparation of trioxane according to the invention is carried out by conversion of homo- and/or copolymers of formaldehyde and if appropriate cyclic formals, for example in the form of a recycling material, in the presence of water and acid catalyst. The amount of water added is measured so that a calculated formaldehyde content of 50 - 90, preferably 65 - 85% by weight is established in the reactor. Addition of foam suppressants may be helpful. Mineral acids, strong organic acids or an amount of another acid catalyst of corresponding catalytic activity are used as the catalyst. Acid catalysts, which in general must be less volatile than the reaction
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- 35

mixture, which have proved to be usable are, in particular, sulfuric acid, phosphoric acid, p-toluenesulfonic acid or strongly acid ion exchangers, for example polystyrene exchangers containing sulfonic acid groups. The amount of catalyst is not critical and is as a rule 1 to 60, preferably 10 - 50% by weight, based on the reaction mixture.

Homo- and copolymers of formaldehyde and/or cyclic formals, preferably copolymers, in comminuted form are employed as the recycling material. The recycling materials can also contain dyestuffs, pigments, stabilizers and other customary additives. The recycling material is metered into the reactor separately, for example via a transfer channel for solids, or together with water. The additives, for example stabilizers, do not interfere with the reaction. The comonomers are also re-formed in the reactor and are worked up together with the trioxane. Separation of the comonomers is prior art. The reaction is carried out according to the invention in a known circulatory reactor with an evaporator. Evaporators which are suitable for this are, for example, forced circulation evaporators, falling film evaporators, rising film evaporators or thin film evaporators with forced circulation. Such systems are described, for example, in Ullmann, Volume 1 (1951), 3rd edition, pages 533 - 537. Forced circulation evaporators are particularly suitable. However, these reactors must contain baffles to prevent the solid particles being sucked up by the pump of the forced circulation reactor. Basket-like baffles or sieves in front of the pumps are suitable for this purpose.

The residence time of the reaction mixture in the reaction system is 5 - 240 minutes, preferably 15 - 60 minutes. The temperature of the reaction mixture is 50 to 150°C, preferably 95 to 130°C, depending on the pressure.

The reaction mixture, which consists of trioxane, formaldehyde and water, and if appropriate cyclic formals, is

removed from the reaction system by distillation with the aid of the evaporator. The reaction here can be carried out under normal pressure, under reduced pressure, for example under 300 to 1000 mbar, or under increased pressure, for example 1 to 4 bar. It is preferably carried out under 1 to 2 bar.

The synthesis vapor which leaves the reaction system is enriched in the customary manner, either as the vapor or as the condensate, by means of rectification, as described in British Patent 1,012,372.

The trioxane-rich fraction obtained, which also contains cyclic formals if appropriate, can be purified, for example, by extraction with a water-immiscible solvent for trioxane (and if appropriate for the cyclic formals), such as methylene chloride, and subsequent neutralization and fractional distillation or crystallization. Other known separation processes can also be used for this purpose (Process Economics Program Stanford Institute Report 23 (1967) 181 or DE-OS 1,570,335). The product streams freed from the trioxane, which still contain chiefly formaldehyde and water, can be recycled continuously into the reaction tank.

The process according to the invention, which can be carried out continuously or discontinuously, makes possible a trioxane synthesis with a minimum energy requirement, since the manufacturing costs for providing highly concentrated formaldehyde are dispensed with. The highly concentrated formaldehyde is replaced here by the recycling material employed. The process represents a contribution to waste disposal and environmental protection, since waste substances are passed to the production process and incineration plants and landfill sites via which the recycling material previously had to be disposed of are therefore relieved.

Examples:

250 g of water, 250 g of concentrated sulfuric acid and 500 g of recycling material in granule form (copolymer of trioxane and 3% by weight of dioxolane) were initially introduced into a 2 l four-necked flask with a stirrer. The mixture was heated to the boiling point and the distillate was condensed in a quench cooler. A further 39 g of granules and 21 g of water (corresponding to a 65% strength formaldehyde solution) were introduced separately into the flask at intervals of in each case 15 minutes. The total reaction time was 5 hours. The composition of the distillate was analyzed hourly. The mean values of the experiments are shown in the table. The dioxolane content corresponds to the comonomer content in the granules employed. The trioxane content in the examples according to the invention corresponds to that obtained from aqueous formaldehyde in the conventional trioxane process according to the prior art (comparison example).

Table

Conditions: Initially introduced into the flask: 250 g of concentrated sulfuric acid; 250 g of water; 500 g of granules

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Temperature: 104°C, running time 5 hours

Feed every $\frac{1}{2}$ hour: 39 g of granules, 21 g of water

Example	Through-put g/h	TOX	CH ₂ O	Dioxolane	Water
		in the dis- tillate %	in the dis- tillate %	in the distillate %	as the difference** %
1	201	25.7	39.8	3.1	31.4
2	223	19.7	40.1	2.4	37.8
Comparison*	250	20.6	41.9	---	37.5

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* Formaldehyde feed concentrations 63.5%, sulfuric acid content in the reactor bottom product 10%

** to make 100%

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of trioxane from formaldehyde, which comprises breaking down an acetal polymer in the presence of water and an acid catalyst and converting the resulting formaldehyde into trioxane in the same process step.
2. The process as claimed in claim 1, wherein a homo- and/or copolymer of formaldehyde and if appropriate cyclic formals is employed as the acetal polymer.
3. The process as claimed in claim 1, wherein a mixture of trioxane and at least one cyclic formal is obtained.
4. The process as claimed in claim 1 or 2 or 3, wherein a recycling material is employed.
5. The process as claimed in claim 1 or 2 or 3, wherein the acetal polymer is a trioxane copolymer with dioxolane/ethylene oxide or with butanediol formal as comonomer constituents.
6. The process as claimed in claim 1 or 2 or 3, which is carried out continuously.
7. The process as claimed in claim 1 or 2 or 3, wherein the reaction is carried out in a forced circulation reactor.
8. The process as claimed in claim 1 or 2 or 3, wherein the reaction temperature is 50 to 150°C.
9. The process as claimed in claim 1 or 2 or 3, wherein the reaction temperature is 95 to 130°C.

10. The process as claimed in claim 1 or 2 or 3, wherein the amount of water is such that the calculated formaldehyde content in the reactor is 50 - 90% by weight.
- 5 11. The process as claimed in claim 1 or 2 or 3, wherein the formaldehyde content is 65 to 85% by weight.
12. The process as claimed in claim 1 or 2 or 3, wherein sulfuric acid, phosphoric acid, p-toluenesulfonic acid or an acid ion exchanger is employed as the acid catalyst in an amount of 1 to 60% by weight, based on the reaction mixture.
- 10 13. The process as claimed in claim 1 or 2 or 3, wherein 10 to 50% by weight of an acid catalyst is employed.
14. The process as claimed in claim 1 or 2 or 3, wherein concentrated sulfuric acid is employed as the catalyst.
- 15 15. The process as claimed in claim 1 or 2 or 3, wherein the reaction products are separated off by distillation under a pressure of 1 to 2 bar.
- 20 16. The process as claimed in claim 1, and substantially as described herein.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente